

## ELECTROCHEMICAL TREATMENT OF Ti6Al4V (1. PART)

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### Abstract

Influence of anodic oxidation (AO) conditions on creation of oxidized layer on Ti6Al4V and its adhesion to substrate was to study. AO was carried out at various voltages, in different electrolytes and at various duration of exposure. TiO<sub>2</sub> nanotubes were created on Ti6Al4V in case of mixed electrolyte. The size of tubes and the thickness of layer slowly increased with increasing DC voltage. The tape test showed that the nanotubular layers treated by AO with/without thermal treatment show a good adhesion to substrate. The effect of AO and thermal treatment to bioactivity will be discussed in the next article.

**Keywords:** surface treatment, Ti6Al4V-alloy, electrochemical oxidation.

### 1 Introduction

Titanium metal and its alloys are used in medicine for their excellent biocompatibility, corrosion resistance and suitable mechanical properties. Titanium is a bioinert material that neither creates a direct bond with bone nor actively induces bone growth. Therefore, various surface modifications have been carried out to improve its bioactivity. For the success of titanium implants not only the bioactivity is a very important precondition but the bond strength of the coating to the titanium substrate and the hardness of this coating are also essential.

Attention has been attracted to the anodic oxidation treatment (AO). Anodic oxidation is a traditional surface modification for preparing oxide films on titanium alloys to improve apatite formation on the surface of implants [1-3]. Anodic oxidation is an electrochemical process, which after application of direct-current voltages to electrodes immersed in electrolyte leads to oxidation of metal anode that forms a solid oxide layer on the surface. The titanium anode oxidizes and TiO<sub>2</sub> is created on the surface.

The type and concentration of electrolyte and the oxidation conditions such as the applied current density, the voltage, the time of oxidation can affect the surface morphology, the chemical composition and the crystalline structure of the oxide films formed by anodic oxidation [1,2,4,5]. Process of anodic oxidation in electrolytes is in progress at low DC voltage (below 20 V) and also at very high voltage (100 - 250 V). The structure of the oxide layer on Ti is typically amorphous at low voltages while crystallization takes place at higher voltages [3,6-9].

In a short time a layer with open pores is formed in acid solutions of H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> and CH<sub>3</sub>COOH and solution of Na<sub>2</sub>SO<sub>4</sub>, of concentration from 0,5 - 2 mol.dm<sup>-3</sup> at high voltage in a

little time. The thickness of the layer increases with increase of voltage. The layer consists of anatase and rutile phases. Between the rutile and apatite structure a lattice matching is and this is important for initiation of the apatite deposition [5-7, 10].

The oxidation process at a low voltage (1-20 V) is well regulated by changes of voltage, duration of process and concentration of electrolytes. The solid oxide layer produced by anodic oxidation can be either compact or nanotubular depending on the anodizing conditions as well as on the composition of electrolytes. If fluoride ions are present in the electrolytes a well nanotubular layer of  $\text{TiO}_2$  can be formed. At the same time except for metal oxidation (during the AO) – partial dissolution of the oxide layer takes place as well [11,12,13].

The oxide layer created on Ti is amorphous at voltages below 20 V. The crystallization of  $\text{TiO}_x$  to rutile and/or anatase phases can be achieved by annealing of the samples at temperatures of 450 – 600 °C. Higher temperatures also stimulate the oxidation. Heat treatment process improves bioactivity of Ti surface [1-3, 11].

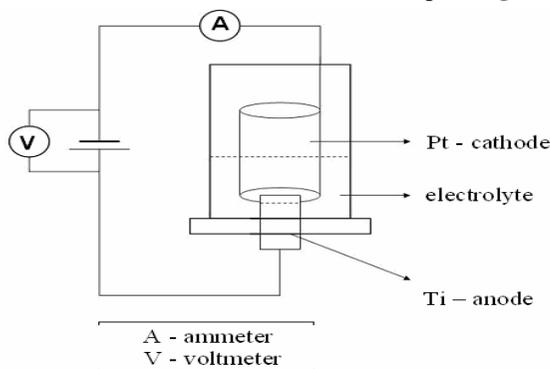
The aim was to prepare a very thin  $\text{TiO}_{2-x}$  layer of a thickness of only several nanometers, which could be bioreactive. The subject of this work was to study the creation of the oxide layer formed on the titanium alloy Ti6Al4V during the electrochemical process at a low voltage and the morphology and mechanical hardness of anodic oxidation layers before and after the thermal treatment.

## 2 Experimental

Experiments were carried out on Ti6Al4V alloys samples of a size of  $10 \times 10 \times 0,8 \text{ mm}^3$ , which were ground by paper No. P 2000, next they were cleaned by ultra-sound in acetone and chloride acid solution (1:1) for 30 min. Then the samples were washed in distilled water and dried in desiccator at room temperature.

The surface of alloys samples were treated by anodic oxidation (AO) in solutions of phosphoric acid of a concentration of  $c(\text{H}_3\text{PO}_4) = 0,5 \text{ mol.l}^{-1}$  and ammonium hydrofluoric of  $c(\text{NH}_4\text{F})=0,135 \text{ mol.l}^{-1}$  and in a solution mix of  $\text{H}_3\text{PO}_4$  and  $\text{NH}_4\text{F}$  ( $c(\text{H}_3\text{PO}_4) = 0,5 \text{ mol.l}^{-1}$  and  $c(\text{NH}_4\text{F})=0,135 \text{ mol.l}^{-1}$ ). The AO process has been made at different direct current voltages of 5 V, 10 V, 15 V and 20 V and the exposure time varied from 5 to 30 minutes. These samples are further marked as AO-sample.

The equipment for AO was constructed from a power supply MPS-3003S MATRIX, an ammeter of sensitivity mA - 30 A, a PE-reaction cell consisting of a Pt-cathode and an anode, which in effected was the Ti6Al4V sample (Fig.1).



**Fig.1** Scheme of anodic oxidation apparatus

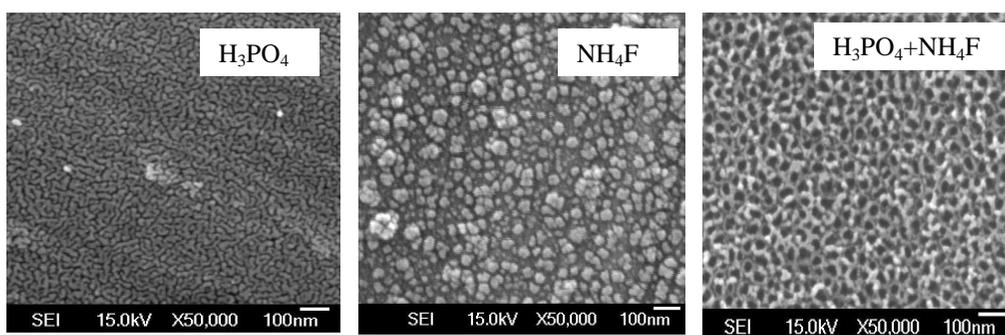
A certain part of the AO-samples in solution mix at a constant voltage of 10 V for 30 minutes were subsequently exposed to thermal treatment by annealing at a temperature of 450°C in duration of 3 hours.

The morphology of the surface oxide layer was studied by electron microscope SEM-EDS (JEOL JSM-7000 F). The thickness of the oxide layer was measured on the fracture of the samples by EM. The weight changes of the samples before and after the anodic oxidation were weighted on Sartorius 4504 MP8-1 scales, with precision  $\pm 0.005$  mg. The cohesion of the oxidized layers and the adhesion of these layers to Ti6Al4V substrate after individual treatments was evaluated by X-cut tape test ASTM D 3359 [14,15]. The extent of surface layer damage after the removal of the Scotch tapes from the samples was observed in detail by SEM-EDS. The mechanical hardness of the tubular layer was tested by nanoindenter ( $^+$ CSM instruments) and punctures were observed by electron microscope.

### 3 Results and discussion

The effect of  $\text{H}_3\text{PO}_4$  ( $0,5 \text{ mol.l}^{-1}$ ),  $\text{NH}_4\text{F}$  ( $c=0,135 \text{ mol.l}^{-1}$ ) and electrolyte mix of  $\text{NH}_4\text{F}$  and  $\text{H}_3\text{PO}_4$  on the oxidation and surface morphology of Ti6Al4V is diverse. The different character of oxide layers, which were created during 20 min of anodic oxidation at a voltage of 10 V, is apparent on **Fig.2**. The results of EDX analysis of surface samples in Table 1 confirm that the surface oxidizes. In the first case the sample weight increases while in the second it decreases. The loss in weight suggests extensive dissolution of Ti6Al4V during the AO-process. Weight losses of samples due to anodic oxidation were measured at application of solutions with  $\text{F}^-$  ions. A relatively great deal of  $\text{F}^-$  ions is incorporated into the oxide layer treated in electrolyte mix.

The surface of the sample treated in  $\text{H}_3\text{PO}_4$  solution was rough and in  $\text{NH}_4\text{F}$  solution generated many unidentified clumps probably amorphous of  $\text{TiO}_x$ . Only in case of treatment of the samples in an electrolyte mix nanotubular structure on the surface was obtained.



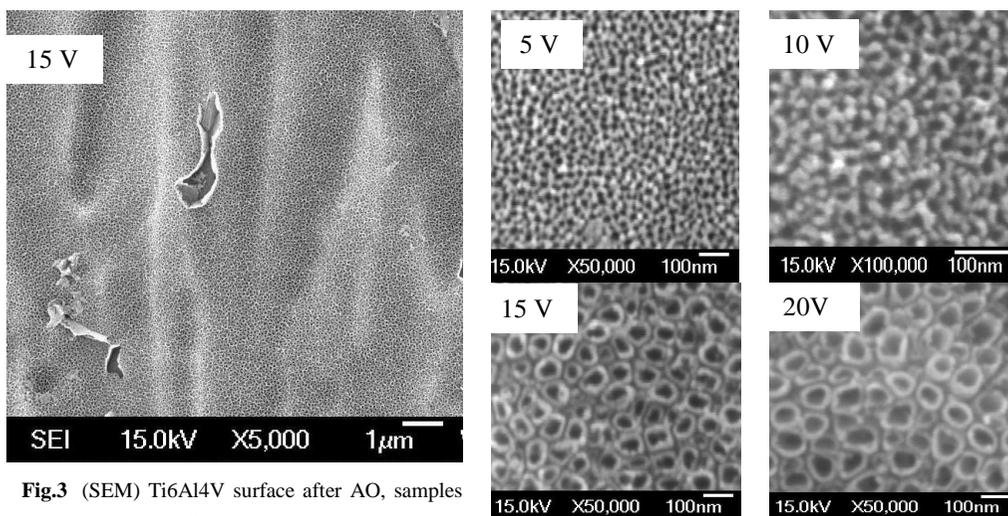
**Fig.2** Fig.2 (SEM) Ti6Al4V surface after AO at condition: voltage 10 V, time 20 min., electrolytes:  $\text{H}_3\text{PO}_4$ ,  $\text{NH}_4\text{F}$  and solution mix of  $\text{H}_3\text{PO}_4+\text{NH}_4\text{F}$

**Table 1** EDX surface analyses and weight-lossing of Ti6Al4V samples after AO at 10V/20min

Conditions of AO	Composition of Ti6Al4V surface after AO [weight %]						Weight-loss [mg. $\text{cm}^{-2}$ ]
	O	F	Al	Ti	V	P	
before AO	0	0	6,0	89,9	4,1	0	-
$\text{H}_3\text{PO}_4$	5,1	0	6,2	86,2	2,6	0	0,012
$\text{NH}_4\text{F}$	2,3	1,2	5,9	87,5	3,0	0	-0,725
solution mix	15,1	8,8	4,7	68,7	2,6	0	-0,322

**The influence of voltage** on the morphology of oxide layers prepared by anodic oxidation in solution mix ( $H_3PO_4+NH_4F$ ) is shown on **Fig. 3**. The effect of the DC voltage was observed in the range of 5 – 20 V. EDX analyses in **Table 2** confirm the oxide layer grows with the increase of voltage. The oxidized layer includes a relatively high amount of atoms of F.

The characters of the oxide layer in case of a 5000-fold magnification seem to be nearly identical. The extension of scans to 50 000 x however display differences of the tube size (**Fig. 3**). The nanotubular layer was created at a voltage above 5 V and at a time of exposition of 30 minutes. In relation to voltage rise a very slow growth of weight loss was recorded in the AO process. The diameter and the length of the tubes increase with voltage because the dissolution is slower than oxidization (**Table 2**). The most homogenous surface was created by electrochemical oxidation in solution mix at a voltage of 10 V. Interestingly the tubes formed at voltages 15 V and 20 V are separated from each other.



**Fig.3** (SEM) Ti6Al4V surface after AO, samples treated for 30 min. in electrolyte mix at voltages of 5V; 10V; 15, 20V.

**Table 2** EDX surface analyses of Ti6Al4V samples treated by AO in electrolyte mix at DC voltages of 5, 10, 15, 20 V for 30 min. and parameters of tubes

Conditions of AO	Composition of Ti6Al4V surface after AO [weight %]					Inner diameter of tubes [nm]	Length of tubes [nm]
	O	F	Al	Ti	V		
5V/30 min	7,1	4,3	5,6	79,6	3,4	10 – 15	80 - 100
10V/30min	15,1	8,8	4,7	68,7	2,6	30 – 40	100 - 130
15V/30min	16,4	6,1	4,8	70,3	2,4	50 – 70	150 - 180
20V/30min	18,7	6,8	4,7	67,3	2,5	50 – 100	180 - 200

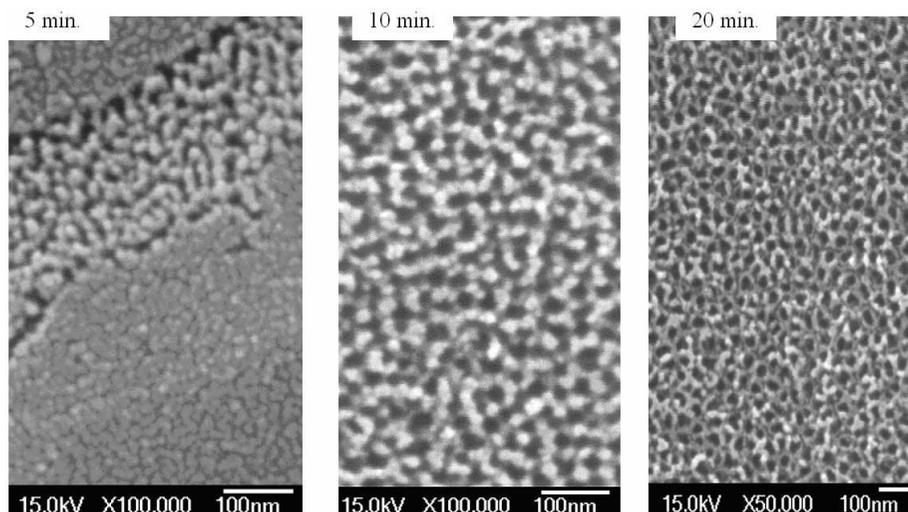
**The effect of the anodizing time** on the character of the layer was studied in AO running 5 to 30 min at a voltage of 10 V in solution mix. As shown in **Fig. 4**, 5 min. for the oxidation process is not enough for the surface to get covered by a uniform nanotubes layer. Practically continuous layer with little holes is evident after 10 min. of anodic oxidation. With increasing of the anodizing time at a constant voltage of 10V a more regular nanotubular structure is created. The

layer is relatively homogenous and smooth and the tubes are arranged close to each other. The chemical compositions of surface and the tube sizes attained after a period of oxidation from 15 to 30 min can be compared in **Table 3**.

**Table 3** EDX surface analyses of Ti6Al4V samples treated by AO in mix electrolyte at different anodic oxidation time and thermally treated

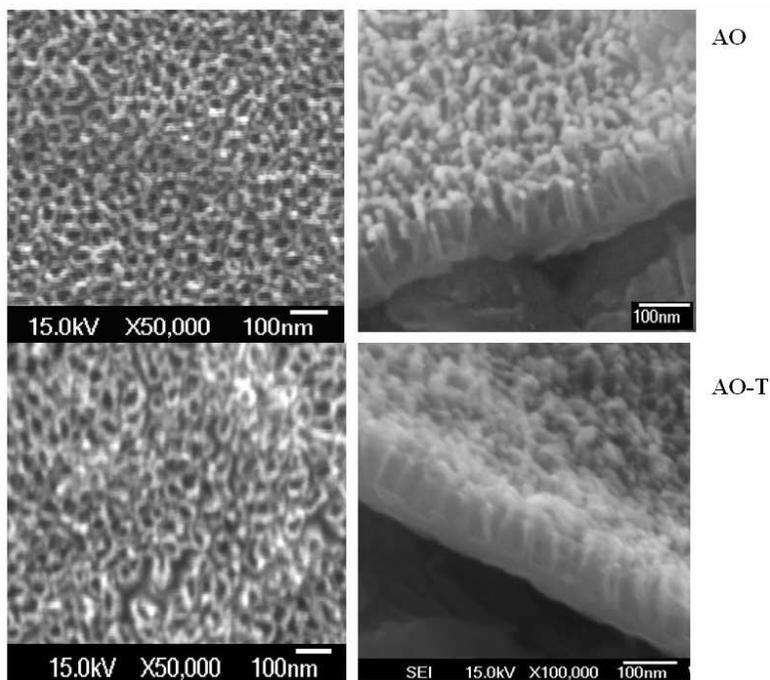
Conditions of AO	Composition of Ti6Al4V surface after AO [weight %]					Inner diameter of tubes [nm]	Length of tubes [nm]
	O	F	Al	Ti	V		
10V/5min	8,6	4,6	4,5	80,1	2,2	10-20	70-80
10V/10min	8,4	4,3	5,3	78,8	3,3	20-40	100-130
10V/15min	9,8	5,0	5,7	77,9	1,6	30-50	120-140
10V/20min	15,8	9,2	4,6	67,6	2,9	40-50	120-150
10V/30min	15,1	8,8	4,7	68,7	2,6	20-40	120-140
AO - 10V/30 min / and annealing T - 450 °C/3 hours	13,3	5,9	5,3	71,8	3,7	-	-

The sizes are practically equivalent, approximately 120 - 140 nm long and of a diameter of about 30 - 50 nm. The length of the tubes and the recorded weight losses of sample confirm that after 15 minutes the AO process is stabilized.



**Fig.4** (SEM) Ti6Al4V surface after AO, samples treated at a voltage of 10V in electrolyte mix for 5, 10 and 20 min

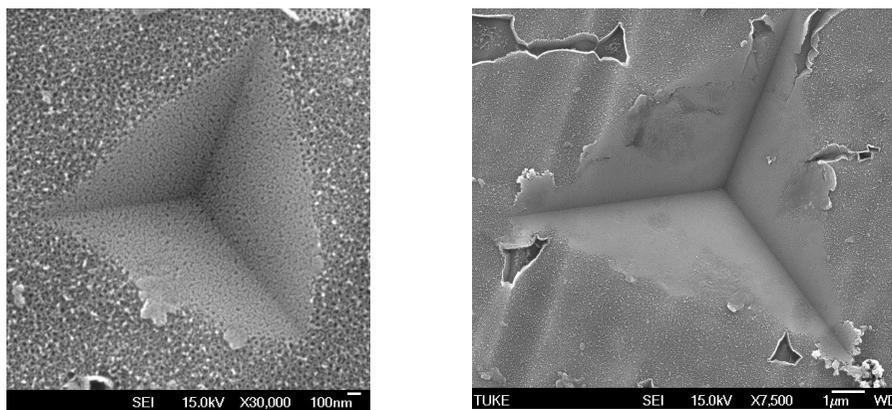
The effect of annealing of AO treated Ti6Al4V at a temperature of 450 °C for 3 hours on the structure of TiO<sub>x</sub> tubes is apparent from **Fig.5**. The annealing causes degradation of tubes. The fracture of the thermal treated sample discovers that the tubes extend to a depth of about 70 nm and the lower part of layer seems to be denser. Although the thickness of layer diminishes the sample weight rises a bit and changes a little the composition of elements in the layer (Table 3). When breaking the sample, the layers separate from each other in a way that one part will contain not only the tubes but also a thin sort of “underlayer” beneath then.



**Fig.5** (SEM) Ti6Al4V surface after AO and the same surface after heat treatment (surface and cross-section)  
 Conditions of AO:  $U = 10V$ ,  $\tau = 30$  min, solution mix; Conditions of annealing:  $t = 450$  °C;  $\tau = 3$  hours.

The measurement of adhesion by tape test showed that the samples prepared by anodic oxidation in a solution mix and prepared by anodic oxidation AO in combination with heat treatment show good adhesion. The nanotubular layer was almost continuously covered with remnants of glue. In areas without glue an intact nanotubular layer was found.

Destruction of tubes after impress of the indenter into deep 250 nm and 2.5  $\mu\text{m}$  is shown in **Fig. 6**. The tubes press together. Penetration resistance increases after penetration of indenter into deep of 100 – 120 nm. The surface of 2,5  $\mu\text{m}$  deep punctures looks like.



**Fig.6** (SEM) Puncture in **nanotubular layer** of the Ti6Al4V treated at conditions of AO:  $U = 10V$ ,  $\tau = 30$  min, solution mix. Deep of puncture  $\approx$  a) 250 nm; b) 2.5  $\mu\text{m}$

#### 4 Conclusions

The results of low DC voltage electrochemical oxidation of Ti6Al4V surface at an extent of 5 to 20 V showed that the character of the oxide layer mostly depends on the electrolyte. Nanotubular layer was obtained only in case of treatment in electrolyte mix  $\text{NH}_4\text{F}$  with  $\text{H}_3\text{PO}_4$ . In case of treatment in  $\text{NH}_4\text{F}$  or  $\text{H}_3\text{PO}_4$  only an amorphous oxide layer was created without tubes. The applied voltage potential and time of exposure at an extent of 5 to 10 V and of 10 to 30 min. did not have a large effect on the character of the tubes layer. With increasing of anodizing time from 10 to 30 min a more regularly nanotubular layer was created with tubes arranged close to each other. The length of tubes was approximately 70 -100 nm and the length and diameter of tubes grows slowly with increase of voltage and exposure time.

As to anodizing time of 5 min at a voltage of 10 V in solution mix it was not enough to create a continuous nanotubular layer. The tubes were separated from each other if the voltage exceeded above 15 V.

The thermal treatment caused degradation of the nanotubular layer. The tape test showed that the thermal treatment does not impair the  $\text{TiO}_x$  layer.

The Ti6Al4V was treated by anodic oxidation and thermal treatment in order to increase its surface reactivity. The surface bioactivity of Ti6Al4V will be studied in the second part of the article.

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